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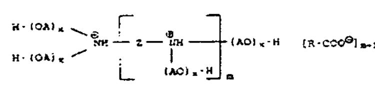
(54) UTILISATION DE SELS D'ACIDE GRAS D'OLIGOAMINES ALCOXYLEES COMME AGENTS AMELIORANTS DU POUVOIR LUBRIFIANT DE PRODUITS PETROLIERS

(54) USE OF FATTY ACID SALTS OF ALKOXYLATED OLIGOAMINES AS LUBRICITY ENHANCERS FOR MINERAL OIL PRODUCTS

(57)

The invention relates to the use of fatty acid salts of alkoxylated oligoamines (I), whereby: A represents alkylene groups having 2 to 8 C atoms; R represents C7 to C23 alkyl groups or monounsaturated or polyunsaturated C7 to C23 alkenyl groups; Z represents C1 to C8 alkylene groupings, C3 to C8 cycloalkylene groupings or C6 to C12 arylene or aryl alkylene groupings; m represents 0 or a whole number ranging from 1 to 5, and the sum of all variables x has a value ranging from 50 % to 300 % of (m+3). Said fatty acid salts of alkoxylated oligoamines are used as lubricity improvers for petroleum products, especially for gasolines and middle distillates.



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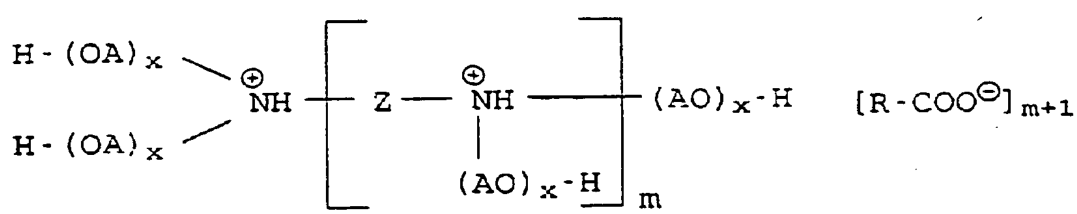

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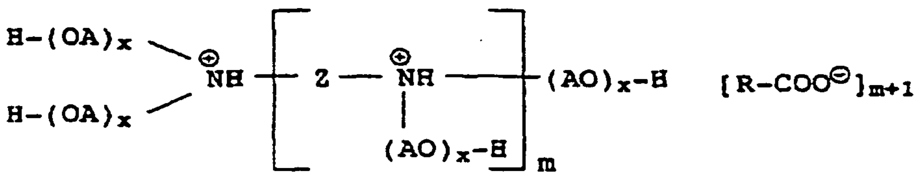
(57) Abrégé/Abstract:
The invention relates to the use of fatty acid salts of alkoxylated oligoamines (I), whereby: A represents alkylene groups having 2 to 8 C atoms; R represents C_7 to C_{23} alkyl groups or monounsaturated or polyunsaturated C_7 to C_{23} alkenyl groups; Z represents C_1 to C_8 alkylene groupings, C_3 to C_8 cycloalkylene groupings or C_6 to C_{12} arylene or aryl alkylene groupings; m represents 0 or a whole number ranging from 1 to 5, and the sum of all variables x has a value ranging from 50 % to 300 % of (m+3). Said fatty acid salts of alkoxylated oligoamines are used as lubricity improvers for petroleum products, especially for gasolines and middle distillates.

Use of fatty acid salts of alkoxylated oligoamines as lubricity enhancers for mineral oil products

Abstract

Fatty acid salts of alkoxylated oligoamines I



(I)

where

A is an alkylene group of 2 to 8 carbon atoms,

R is C_7- to C_{23}-alkyl or mono- or polyunsaturated C_7- to C_{23}-alkenyl,

Z is a C_1- to C_8-alkylene group, C_3- to C_8-cycloalkylene group or C_6- to C_{12}-arylene or arylalkylene group,

m is 0 or an integer from 1 to 5 and

the sum of all variables x is from 50 to 300% of (m+3),

are used as lubricity enhancers for mineral oil products, in particular for gasoline fuels and middle distillates.

Use of fatty acid salts of alkoxylated oligoamines as lubricity enhancers for mineral oil products

The present invention relates to the use of fatty acid salts of alkoxylated oligoamines as lubricity enhancers for mineral oil products, in particular for gasoline fuels and middle distillates, especially diesel fuels, and additive concentrates for such mineral oil products and such mineral oil products themselves which contain these fatty acid salts of alkoxylated oligoamines.

Carburettors and intake systems of gasoline engines, but also injection systems for fuel metering, are increasingly becoming contaminated by impurities due to dust particles from the air, uncombusted hydrocarbon residues from the combustion chamber and the crank case vent gases passed into the carburretor.

These residues shift the air/fuel ratio during idling and in the lower part-load range in such a way that the mixture becomes leaner, the combustion more incomplete and in turn the amounts of uncombusted or partially combusted hydrocarbons in the exhaust gas become larger and the gasoline consumption increases.

It is known that these disadvantages can be avoided by using fuel additives for keeping valves and carburretors or injection systems for gasoline engines clean (cf. for example: M. Rossenbeck in Katalysatoren, Tenside, Mineralöladditive, Editors J. Falbe, U. Hasserodt, page 223, G. Thieme Verlag, Stuttgart 1978).

Such fuel additives (detergents) which maintain cleanliness and can derive from a large number of classes of chemical substances, such as polyalkeneamines, polyetheramines, polybutene Mannich bases or polybutenylsuccinimides, are used in general in combination with carrier oils and in some cases further additive components, such as corrosion inhibitors and demulsifiers.

However, gasoline fuels with and without such additive components generally exhibit inadequate behavior in need of improvement, with regard to their lubricity and antiwear properties in gasoline engines.

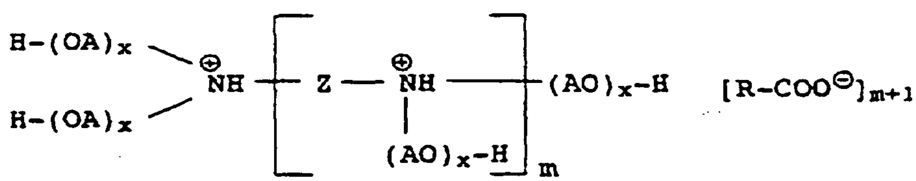
The low-sulfur diesel fuel increasingly used nowadays also gives rise to lubricity problems which result, for example, in greater wear in the injection pumps. The reduction of the sulfur content in diesel fuels is required for reducing or avoiding

sulfur-dioxide and particle emissions. To achieve lower sulfur contents, the diesel fuels must be hydrogenated. As a result, polar and polynuclear aromatic components in the fuel, which are responsible for the natural lubricating effect of the diesel fuel, are also destroyed. Here too, as in the case of the gasoline fuels, there is therefore a need for additives which sufficiently increase the lubricity in the fuel (also referred to as lubricity additive or friction modifier).

Lubricity-enhancing additives known to date for gasoline fuel are, for example, fatty acids, as described, for example in WO 98/11175, alkenylsuccinic esters, bis(hydroxyalkyl)-fatty amines and hydroxyacetamides. For diesel fuels, in particular fatty acids and fatty acid derivatives, for example esters of glycerol with unsaturated fatty acids, or castor oil, as described in EP-B 605 857, are used as lubricity-enhancing additives.

However, since said prior art materials are unsatisfactory in their property profile, in particular with regard to their lubricating and antiwear effect, it is an object of the present invention to provide more efficient lubricity enhancers for mineral oil products, in particular for gasoline fuels and middle distillates.

We have found that this object is achieved by the use of fatty acid salts of alkoxylated oligoamines of the formula I



(I)

where

A is an alkylene group of 2 to 8 carbon atoms,

R is C_7- to C_{23}-alkyl or mono- or polyunsaturated C_7- to C_{23}-alkenyl, which may additionally carry hydroxyl groups,

Z is a C_1- to C_8-alkylene group, C_3- to C_8-cycloalkylene group or C_6- to C_{12}-arylene or arylalkylene group,

m is 0 or an integer from 1 to 5 and

CA 02388065 2002-04-18

the sum of all variables x has a value of from 50 to 300% of (m+3), as lubricity enhancers for mineral oil products.

Said compounds of the formula I are already known as such. US 4 131 583 describes salts of, in particular, unsaturated C_{11}- to C_{20}-carboxylic acids with N,N,N',N'-tetrahydroxyethyl-C_2-C_4-alkylenediamines, these are recommended exclusively as corrosion inhibitors in aqueous coating materials for metal surfaces.

JP-A 11/050076 discloses that N,N,N',N'-tetrakis(2-hydroxypropyl) ethylenediamine in the presence of fatty acids, such as stearic acid or oleic acid, in aqueous lubricating oil compositions, such as cutting oil or milling oil, prevents rust formation and fungal attack and stabilizes the composition. An improvement of the lubricating effect is not mentioned therein.

JP-A 11/209773 discloses aqueous lubricants for conveyor belts in the filling of bottles with beverages, which lubricants contain fatty acid salts of alkanolamines, such as N,N,N',N'-tetrakis(2-hydroxypropyl)ethylenediamine. For example, palmitic acid, tetradecanoic acid, oleic acid and lauric acid are mentioned as fatty acids.

Mineral oil products are to be understood here as meaning power fuels, operating materials, combustion fuels and lubricating oils, which however are based not only on mineral oil but also partially or completely on synthetic and/or naturally occurring raw materials. Examples of such raw materials are natural gas, methanol, ethanol, coal liquefaction products or rapeseed oil, which are processed to give fuels or incorporated in fuels based on mineral oil. The designated mineral oil products are as a rule virtually anhydrous or contain water at least only in minor amounts. Examples of water-containing mineral oil products are fuel emulsions, such as diesel/water emulsions, which may usually contain up to about 35% by weight of water. Mineral oil products preferred for the present invention are on the one hand gasoline fuels and on the other hand middle distillates, in particular diesel fuels.

The alkylene group A is preferably derived from corresponding alkylene oxides, such as ethylene oxide, 1,2-propylene oxide, 1,2-butylene oxide and cis- or trans-2,3-butylene oxide. However, they may also be 1,3-propylene, 1,4-butylene, 1,6-hexylene or 1,8-octylene. A may likewise be a mixture of different groups

from among said groups. A is particularly preferably an ethylene, 1,2-propylene or 1,2-butylene group.

The relatively long-chain radical R occurring in the carboxylate anion is, for example, branched or preferably linear C_7- to C_{23}-alkyl, preferably C_{11}- to C_{21}-alkyl, especially C_{15}- to C_{19}-alkyl, which may additionally carry hydroxyl groups. Examples of parent carboxylic acids are octanoic acid, 2-ethylhexanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid (lauric acid), tridecanoic acid, isotridecanoic acid, tetradecanoic acid (myristic acid), hexadecanoic acid (palmitic acid), octadecanoic acid (stearic acid) and eicosanoic acid. Said acids may be of natural or synthetic origin. The carboxylate anions may also be based on mixtures of said acids.

The relatively long-chain radical R occurring in the carboxylate anion is however preferably a mono- or polyunsaturated C_7- to C_{23}-radical, in particular mono- or polyunsaturated C_{11}- to C_{21}-alkenyl, especially C_{15}- to C_{19}-alkenyl, which may additionally carry hydroxyl groups. These unsaturated radicals are preferably linear. In the case of polyunsaturated alkenyl groups, they preferably contain two or three double bonds. Examples of parent carboxylic acids are elaidic acid, ricinoleic acid, linoleic acid and linolenic acid. Particularly good results are obtained with oleic acid. The carboxylate anions may also be based on mixtures of such unsaturated carboxylic acids with one another and also with the abovementioned saturated carboxylic acids. Such mixtures are, for example, tall oil, tall oil fatty acid and rapeseed oil fatty acid. Said unsaturated carboxylic acids and said mixtures are as a rule of natural origin.

Z is in particular a C_1- to C_4-alkylene group, such as methylene, 1,2-propylene, 1,2-butylene, 1,3-butylene or 2,3-butylene, C_5- to C_6-cycloalkylene group, such as 1,3-cyclopentylidene or 1,3- or 1,4-cyclohexylidene or C_6- to C_8-arylene or arylalkylene group, such as 1,3- or 1,4-phenylene, 2-methyl-1,4-phenylene or 1,3- or 1,4-bismethylenephenylene.

Z is however preferably a polymethylene group of the formula $-(CH_2)_n-$ where n is from 2 to 8, in particular from 2 to 6, i.e. in particular 1,2-ethylene, 1,3-propylene, 1,4-butylene, 1,5-pentylene and 1,6-hexylene, but also 1,7-heptylene and 1,8-octylene.

m is 0, the fatty acid salts used according to the invention are as a rule, dependent on the sum (Σ) of all variables x, based on mixtures of mono-, di- and/or trialkanolamines or pure

trialkanolamines as cationic components. Examples of such alkanolamines are monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, triisopropanolamine and the associated mixtures. In this group, the oleic acid salt of triethanolamine ($\Sigma x = 3$) is of particular interest.

m is however preferably 1 or 2. For m = 1, completely and/or partially alkoxylated alkylenediamines such as 1,2-ethylenediamine, 1,3-propylenediamine or 1,4-butylenediamine, form the basis. For m = 2, in general completely and/or partially alkoxylated dialkylenetriamines such as di(1,2-ethylene)triamine, di(1,3-propylene)triamine or di(1,4-butylene)triamine, form the basis. In this group, the bisoleic acid salts of N,N,N',N'-tetrakis(2'-hydroxyethyl)-1,2-ethylenediamine ($\Sigma x = 4$) and N,N,N',N'-tetrakis(2'-hydroxypropyl)-1,2-ethylenediamine ($\Sigma x = 4$) and the trisoleic acid salts of di(1,2-ethylene)triamine reacted with from 4 to 5 mol of ethylene oxide or 1,2-propylene oxide are of particular interest.

However, it is also possible to use higher homologues of said alkylenediamines and dialkylenetriamines, for example tetraethylenetetramine (m = 3), tetraethylenepentamine (m = 4) or pentaethylenehexamine (m = 5), as parent amine components for the fatty acid salts used according to the invention.

The number of alkylene oxide units (OA) introduced per amine molecule may correspond to the number of N-H bonds in the parent amine ($\Sigma x = m+3$). However, it is also possible to incorporate more or less OA units. In the case of superstoichiometric incorporation, triple alkoxylation per N-H bond [300% of (m+3)] is an upper limit with respect to the properties of the resulting fatty acid salts. In the case of substoichiometric incorporation, 50% alkoxylation on average [50% of (m+3)] is a corresponding lower limit; here, mixtures of species having different degrees of alkoxylation are then generally present.

In a preferred embodiment, the sum (Σ) of all variables x has a value of from 75 to 125% of (m+3).

The fatty acid salts used according to the invention and of the formula I can usually be easily prepared by alkoxylation of the parent amines by conventional methods and subsequent neutralization with the fatty acids of the formula R-COOH.

When C_2- to C_4-alkylene oxides are used, the alkoxylation is expediently carried out in the presence of small amounts of water (at most from 0.5 to 5% by weight, based on the amount of amine used), without a catalyst, at from 80 to 140°C, for the introduction of the first alkylene oxide unit into the N-H bond, and the absence of water, in the presence of basic catalysts, such as alkali metal hydroxides, e.g. sodium hydroxide or potassium hydroxide, at from 100 to 150°C, for the introduction of further alkylene oxide units.

The neutralization is carried out as a rule by heating the alkoxylated amines obtained with the corresponding stoichiometric or slightly substoichiometric amount (i.e. from 90 to 100%, in particular from 95 to 100%, of theory) of fatty acid to temperatures of from 30 to 100°C, in particular from 40 to 80°C, for from 15 minutes to 10 hours, in particular from 30 minutes to 5 hours. The neutralization reaction should be carried out in such a way that no carboxylic ester fractions result in the product. In many cases, both the alkoxylated amine and the fatty acid can be used in the form of liquids, which makes the reaction to the corresponding fatty acid salt particularly simple. The order in which alkoxylated amine and fatty acid are combined is not critical, either the alkoxylated amine can be initially taken and the fatty acid added or the fatty acid can be initially taken and the alkoxylated amine added.

However, it is in principle also possible to add the alkoxylated amine and the fatty acid as individual components to the additive concentrates or the mineral oil products and to allow the salt formation to take place there.

The preparation of the fatty acid salts used according to the invention and of the formula I generally requires substantially less effort and energy than in the case of conventional lubricity enhancers of the prior art, in particular those based on amides or esters, in the preparation of which higher temperatures, longer reaction times and expensive working-up procedures precipitating off undesired byproducts, which occur in particular in the case of condensation reactions, are as a rule required.

The described fatty acid salts of the formula I are very suitable as lubricity enhancers (lubricity additives, lubricity modifiers) in mineral oil products, in particular in gasoline fuels and in middle distillates, especially diesel fuels. The fatty acid salts I are in general highly efficient and hence widely usable. Where fatty acid salts I are used, the tendency for wear to occur in

the parts of the machines and units operated with the mineral oil products is substantially reduced.

The fatty acid salts used according to the invention in gasoline fuels and of the formula I can be advantageously used in combination with, in principle, all conventional gasoline fuel additives.

Examples of conventional gasoline fuel additives having a detergent effect are:

(a) polyisobuteneamines which are obtainable according to EP-A 244 616 by hydroformylation of highly reactive polyisobutene having a number average molecular weight of from 300 to 5000 and subsequent reductive amination with ammonia, monoamines or polyamines, such as dimethyleneaminopropylamine, ethylenediamine, diethylenetriamine, triethylenetetramine or tetraethylenepentamine;

(b) poly(iso)buteneamines which are obtainable by chlorination of polybutenes or polyisobutenes having double bonds predominantly in the β- and γ-position and subsequent amination with ammonia, monoamines or the polyamines mentioned above under (a);

(c) poly(iso)buteneamines which are obtainable by oxidation of double bonds in poly(iso)butenes with air or ozone to give carbonyl or carboxyl compounds and subsequent amination under reducing (hydrogenating) conditions;

(d) polyisobuteneamine which are obtainable according to DE-A 196 20 262 from polyisobutene epoxides by reaction with amines and subsequent dehydration and reduction of the amino alcohols;

(e) polyisobuteneamines which may contain a hydroxyl group and which are obtainable according to WO-A 97/03946 by reaction of polyisobutenes having an average degree of polymerization P of from 5 to 100 with oxides of nitrogen or mixtures of oxides of nitrogen and oxygen and subsequent hydrogenation of these reaction products;

(f) hydroxyl-containing polyisobuteneamines which are obtainable according to EP-A 476 485 by reaction of polyisobutene epoxides with ammonia, monoamines or the abovementioned polyamines;

(g) polyetheramines which are obtainable by reaction of C_2- to C_{30}-alkanols, C_6- to C_{30}-alkanediols, mono-, di- or tri-C_2- to C_{30}-alkylamines, C_1- to C_{30}-alkylcyclohexanols or C_1- to C_{30}-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl or amino group and subsequent reductive amination with ammonia, monoamines or the abovementioned polyamines; such products also have carrier oil properties;

(h) polyisobutene Mannich bases which are obtainable in particular according to EP-A 831 141 or according to German Patent Applications 199 48 111.3 and 199 48 114.8 by reaction of polyisobutene-substituted phenols with aldehydes and monoamines of the abovementioned polyamines;

(i) polypropyleneamines according to WO 94/24231, which are obtainable by metallocene-catalyzed propene oligomerization and, subsequently, the hydroformylation and reductive amination steps stated above under (a);

(j) additives containing carboxylic ester groups, preferably based on esters of mono-, di- or tricarboxylic acids with long-chain alcohols or polyols, in particular those having a minimum viscosity of 2 mm^2/s at 100°C, as described in DE-A 38 38 918; adipates, phthalates, isophthalates, terephthalates and trimellitates of isooctanol, of isononanol, of isodecanol and of isotridecanol may be mentioned as examples here; such products also have carrier oil properties;

(k) imides, amides, esters and ammonium and alkali metal salts of polyisobutenylsuccinic anhydrides which are obtainable from conventional or highly reactive polyisobutene and maleic anhydride by a thermal method or via chlorinated polyisobutene and can be used in particular in the form of the derivatives with aliphatic polyamines; such gasoline fuel additives are described in particular in US-A 4 849 572.

Examples of conventional gasoline fuel additives which inhibit valve seat wear are:

(l) additives containing carboxyl groups or their alkali metal or alkaline earth metal salts, in particular the copolymers of C_2-C_{40}-olefins with maleic anhydride, which are described in EP-A 307 815 and have a total molar mass of from 500 to 20,000 and some or all of whose carboxyl groups have been reacted to give the alkali metal or alkaline earth metal salts and a remainder of the carboxyl groups have been reacted with alcohols or amines;

(m) additives containing sulfo groups or their alkali metal or alkaline earth metal salts, in particular the alkali metal or alkaline earth metal salts of alkyl sulfosuccinates, which salts are described in EP-A 639 632.

In addition to and together with said gasoline fuel additives (a) to (m), further conventional carrier oils, additive components and assistants may be combined with the fatty acid salts of the formula I for use in gasoline fuels.

Examples of conventional carrier oils for gasoline fuel additives are mineral carrier oils (base oils), in particular those of viscosity class "Solvent Neutral (SN) 500 to 2000", synthetic carrier oils based on olefin polymers having M_N = 400 to 1800, especially based on polybutene or polyisobutene (hydrogenated or unhydrogenated), and on poly-alphaolefins or poly-internal-olefins, and synthetic carrier oils based on alkoxylated long-chain alcohols or phenols. Mixtures of said carrier oils can of course also be used.

Fractions obtained in mineral oil processing such as kerosine, naphtha or brightstock, are also suitable as mineral carrier oils and/or diluents or solvents for gasoline fuel additives. Aromatic hydrocarbons, paraffinic (aliphatic) hydrocarbons and alkoxyalkanols are furthermore suitable for this purpose.

Of particular importance here as carrier oils for gasoline fuel additives are polyetherols which are obtainable by reaction of C_2- to C_{30}-alkanols, C_6- to C_{30}-alkanediols, mono-, di- or tri-C_2- to C_{30}-alkylamines, C_1- to C_{30}-alkylcyclohexanols or C_1- to C_{30}-alkylphenols with from 1 to 30 mol of ethylene oxide and/or propylene oxide and/or butylene oxide per hydroxyl or amino group. Particular examples here are alcohol-initiated polyetherols having from about 10 to 35, in particular from 15 to 30, propylene oxide and/or butylene oxide units; particularly suitable initiator alcohols here are linear or branched C_6- to C_{15}-alkanols.

Further conventional additive components and assistants for gasoline fuel are corrosion inhibitors, for example based on ammonium salts of organic carboxylic acids, which salts tend to form films, or heterocyclic aromatics in the case of corrosion protection of nonferrous metals, antioxidants or stabilizers, for example based on amines such as p-phenylenediamine, dicyclohexylamine or derivatives thereof or on phenols, such as 2,4-di-tert-butylphenol or 3,5-di-tert-butyl-4-hydroxyphenylpropionic acid, demulsifiers, antistatic agents, metallocenes, such as ferrocene or methylcyclopentadienylmanganesetricarbonyl, and markers. Medium-chain linear or branched alkanols (having, for example, from 6 to 12 carbon atoms), e.g. 2-ethylhexanol, are often used as solubilizers. Amines are sometimes also added for lowering the pH of the fuel.

The fatty acid salts used according to the invention in gasoline fuels and of the formula I can also be employed together with other lubricity enhancers customary for this purpose, such as specific fatty acids, alkenylsuccinic esters, bis(hydroxyalkyl)-fatty-amines or hydroxyacetamides.

The carboxylic acids or fatty acids used as corrosion inhibitors or lubricity enhancers may be present as monomeric or oligomeric, in particular dimeric species. Mixtures of monomeric and dimeric and, if required, higher oligomeric species may also be present.

Combinations of the fatty acid salts used according to the invention in gasoline fuels and of the formula I with the detergents of the abovementioned groups (a), (d) and (g), in particular with polyisobuteneamines of group (a), are preferred. Particularly suitable polyisobuteneamines (a) here are those which are prepared by hydroformylation of highly reactive polyisobutenes having a number average molecular weight of from 500 to 2300, in particular from 800 to 1500, especially from 900 to 1200, and subsequent reductive amination with ammonia. The polyisobuteneamines (a) are preferably used together with carrier oils, for example polyetherols or aliphatic or aromatic hydrocarbons, and, if required, with the abovementioned corrosion inhibitors, antioxidants or stabilizers, demulsifiers, antistatic agents, metallocenes and/or markers. A typical example of such a polyisobuteneamine (a) is the product sold under the tradename Kerocom® PIBA by BASF Aktiengesellschaft.

Suitable gasoline fuels are all commercial gasoline fuel compositions. A typical example here is the commercial Eurosuper base fuel according to EN 228. The gasoline fuel composition

described in German Patent Application 199 05 211.5 is also of interest here.

The fatty acid salts used according to the invention in middle distillates and of the formula I can advantageously be used in all conventional middle distillates.

These middle distillates, of which diesel fuels constitute the most important group, include refined mineral oil products which usually have a boiling range from 100 to 400°C. These are generally distillates having a 95% point up to 360°C or higher. However, they may also be ultra low sulfur diesel or city diesel, characterized by a 95% point of, for example, not more than 345°C and a sulfur content of not more than 0.005% by weight or by a 95% point of, for example, 285°C and a sulfur content of not more than 0.001% by weight. Moreover, these middle distillates may also be heating oils having a sulfur content of not more than 0.20, in particular, not more than 0.10, % by weight, and aviation fuels.

Said distillates are usually composed of components which are obtained from the distillation of mineral oil under atmospheric or reduced pressure or are obtained from conversion processes, for example cracker, coker or visbreaker gas oil.

Said middle distillates, especially diesel fuels, are distinguished by a low sulfur content, as a rule not more than 0.05, in particular not more than 0.02, especially not more than 0.005, very particularly preferably not more than 0.001, % by weight.

The fatty acid salts used according to the invention in middle distillates, especially diesel fuels, and of the formula I can be incorporated herein as pure liquid substances or as liquid concentrates in a solvent or diluent. In principle, all substances stated above as such compositions for use with gasoline fuel additives can be used here as solvents or diluents. Mineral oil fractions such as naphtha, kerosine, diesel fuel and aromatic hydrocarbons, such as heavy solvent naphtha, Solvesso® or Shellsol® are particularly suitable. These concentrates may be solutions or dispersions, clear solutions being preferred. Mixtures of said solvents or diluents may also be used.

By using said solvents or diluents, in particular in a weight ratio to the fatty acid salts I of from 1:10 to 10:1, in particular from 1:4 to 4:1, especially from 1:2 to 2:1, the solubility of the fatty acid salts used according to the

invention and of the formula I can be improved. Such solutions or dilutions are advantageous when the middle distillate already contains further additives, when the mixing-in temperatures are low, when the metering means is not tailored to low doses or when mixtures with other middle distillates are to be prepared.

The fatty acid salts used according to the invention in middle distillates and of the formula I can advantageously be employed in combination with in principle all conventional middle distillate or diesel fuel additives.

Conventional middle distillate or diesel fuel additives in this context are in particular detergents, corrosion inhibitors, dehazers, demulsifiers, antifoams, antioxidants, metal deactivators, multifunctional stabilizers, cetane number improvers, combustion improvers, dyes, markers, solubilizers, antistatic agents, other conventional lubricity additives and the additives which improve low temperature properties, such as flow improvers (MDFI), paraffin dispersants (WASA) and the combination thereof (WAFI).

The present application also relates to a process for improving the lubricity of mineral oil products, in particular gasoline fuels and middle distillates, wherein effective amounts of fatty acid salts of alkoxylated oligoamines of the formula I 1 to 6 [sic] are added to the mineral oil products.

The present invention furthermore relates to additive concentrates for mineral oil products, in particular for gasoline fuels and middle distillates, which contain the fatty acid salts of alkoxylated oligoamines of the formula I in amounts of from 0.05 to 50, in particular from 0.1 to 30, % by weight, based on the total amount of the concentrates. These concentrates usually also contain the abovementioned further additives, carrier oils, solvents or diluents and/or assistants. In the case of additive concentrates for gasoline fuels, these are in particular detergents and/or compositions inhibiting valve seat wear, especially the abovementioned additives (a) to (m), and further components and assistants customary for this purpose, in particular carrier oils, corrosion inhibitors, antioxidants or stabilizers, demulsifiers, antistatic agents, metallocenes and markers.

The present invention furthermore relates to mineral oil products, in particular gasoline fuel and middle distillate compositions, which contain the fatty acid salts of alkoxylated oligoamines of the formula I in effective amounts. Effective

amounts are as a rule to be understood, both in the case of gasoline compositions and in the case of diesel fuel compositions, as meaning from 1 to 1000, in particular from 5 to 500, especially from 10 to 250, particularly preferably from 20 to 100, ppm by weight, based in each case on the total amount of the composition. These mineral oil products, in particular the gasoline fuel and middle distillate compositions, usually contain the abovementioned additives, additive components and assistants in addition to the fatty acid salts I used according to the invention in them.

The fatty acid salts of alkoxylated oligoamines of the formula I are highly effective as lubricity enhancers even in low concentrations in the mineral oil products and effectively protect wear in those parts of the machines and assemblies operated with the mineral oil products, for example in fuel intake systems or injection pumps.

Furthermore, the fatty acid salts of alkoxylated oligoamines of the formula I have good compatibility with lubricating oil, which is important in particular when used in diesel fuels. As a result of the interaction of acidic lubricity enhancers (such as dimeric fatty acids), used to date, with basic components of lubricating oil, which are known to be in contact with the fuel in gasoline and diesel engines, corresponding salts may be deposited in the fuel and on undesired areas of the engine or of the injection system and may give rise to faults. This disadvantage is avoided by the novel use of the fatty acid salts of alkoxylated oligoamines of the formula I.

Furthermore, the fatty acid salts of alkoxylated oligoamines of the formula I, which salts are used according to the invention, have virtually no tendency to undesired emulsion formation in the mineral oil products and are sufficiently stable to hydrolysis.

The examples which follow illustrate the invention without restricting it.

Preparation Examples

Example 1: Preparation of the bisoleic acid salt of N,N,N',N'-tetrakis(2'-hydroxypropyl)-1,2-ethylenediamine

58.4 g (0.2 mol) of N,N,N',N'-tetrakis(2'-hydroxypropyl)-1,2-ethylenediamine (prepared by conventional reaction of 1,2-ethylenediamine with 4 mol of propylene oxide in the presence of about 3% by weight, based on the amount of the amine used, of

water, at from 100 to 110°C) were heated to 60-80°C and mixed with 110.4 g (0.4 mol) of oleic acid in the course of 2 hours while stirring. During this procedure, the pH did not fall below 7. Stirring was then carried out for a further 2 hours in the stated temperature interval. The product obtained had an N titer of 2.39 mmol/g (calculated 2.37 mmol/g).

Example 2: Preparation of the bisoleic acid salt of N,N,N',N'-tetrakis(2'-hydroxyethyl)-1,2-ethylenediamine

The title compound was prepared analogously to Example 1 using the analogous amounts of N,N,N',N'-tetrakis(2'-hydroxyethyl)-1,2-ethylenediamine.

Use Examples

Example 3: Determination of the fretting values in gasoline fuel

To test the lubricity or the wear in gasoline fuels, a high frequency reciprocating rig (HFRR) apparatus from PCS Instruments, London was used. The measuring conditions were adapted to the use of gasoline fuels. The applicability of this test method to gasoline fuel is demonstrated by the publications D. Margaroni, Industrial Lubrication and Tribology, Vol. 50, No. 3, May/June 1998, pages 108-118, and W. D. Ping, S. Korcek, H. Spikes, SAE Techn. Paper 962010, pages 51-59 (1996).

The gasoline fuel (GF) used here (typically gasoline fuel according to EN 228) were evaporated down to 50% by volume by distillation under mild conditions for the measurements. This 50% residue was used in the test in the wear measuring apparatus for determining the blank value. Further additives were added to this residue according to the examples shown below, and the fretting values was [sic] determined according to the abovementioned method. The resulting fretting values (F) are stated in micrometers (μm); the lower this value, the lower is the resulting wear.

The 50% by volume residue of a Eurosuper gasoline fuel GF1 gave a blank value of F = 873 μm in the HFRR test, while a 50% by volume residue of a comparable Eurosuper gasoline fuel GF2 gave a blank value of F = 754 μm in the HFRR test. The addition of 500 mg/kg of a commercial gasoline fuel additive package P1 (based on a polyisobuteneamine detergent, a synthetic carrier oil and a conventional corrosion inhibitor) or a commercial gasoline fuel additive package P2 (analogous to P1 but with another synthetic carrier oil) to the said residue in each case led to fretting

values of the same order of magnitude. The addition of in each case 50 mg/kg of the novel lubricity enhancers from Examples 1 and 2 or of the lubricity enhancers known from the prior art resulted in correspondingly lower values, the novel products being in general substantially superior to those of the prior art. The values obtained are shown below in table 1.

Table 1: Fretting values F in gasoline fuel

Additive introduced	GF	R [∝m]
None	GF1	873
500 mg/kg of package P1	GF1	853
500 mg/kg of package P1 + 50 mg/kg of product from Example 2	GF1	686
none	GF2	754
500 mg/kg of package P1	GF2	717
500 mg/kg of package P1 + 50 mg/kg of product from Example 1	GF2	593
500 mg/kg of package P1 + 50 mg/kg of product from Example 2	GF2	634
500 mg/kg of package P1 + 50 mg/kg of comparative product	GF2	659
500 mg/kg of package P2	GF2	775
500 mg/kg of package P2 + 50 mg/kg of product from Example 1	GF2	680
500 mg/kg of package P2 + 50 mg/kg of product from Example 2	GF2	633
500 mg/kg of package P2 + 50 mg/kg of comparative product	GF2	684

In each case a commercial lubricity enhancer based on tall oil fatty acid and according to WO 98/11175 was used as the comparative product.

Example 4: Determination of the fretting values in diesel fuels

Standard lubricity tests were carried out using an HFRR apparatus from PCS Instruments, London, in which a steel ball rubs against a steel plate in the test fuel. ISO 12156-1 describes this method and has been introduced into the diesel standard EN 590-1999. The limit specified here is an abrasion on the steel ball of not more than 460 µm. Low-sulfur diesel fuels without additives may have fretting values F of, typically, from 400 to 700 µm.

The test diesel fuels (DF1 to DF4) stated in Table 2 below had the stated characteristics.

Table 2: Characteristics of the test diesel fuel

		DF 1	DF 2	DF 3	DF 4
Quality	[mg/kg]	EN 590	EN 590	EN 590	C-DK MK 1
Sulfur content	[kg/m^3]	180	700	430	6
Density	[°C]	841.3	835.6	830.6	810.6
CP	[°C]	-6	-6	-7	-31
CFPP	[°C]	-9	-10	-10	-32
Initial boiling point	[°C]	170	176	175	184
20% by volume	[°C]	235	214	218	219
95% by volume	[°C]	363	352	343	280
Final boiling point	[°C]	371	370	356	289

The sulfur content was determined according to EN ISO 14 596.

The following diesel fuel additives were used:

Additive A:
product from Example 2, used according to the invention (undiluted)

Additive B:
product from Example 1, used according to the invention (undiluted)

Additive C:
as a comparison, commercial lubricity enhancer based on a mixture of a sterically hindered alkylphenol and a long-chain carboxylic acid

Additive D:
as a comparison, commercial lubricity enhancer based on a mixture of a carboximide and a natural fatty ester

Additive E:
as a comparison, commercial lubricity enhancer based on a mixture of glyceryl monooleate and glyceryl monolinolate

Additive F:
as a comparison, commercial lubricity enhancer based on a mixture of long-chain carboxylic acids

Table 3 below shows the results of the determination of the fretting values F in the test diesel fuels. It is clear that the effect of the products A and B used according to the invention is superior to that of the commercial products C to F.

Table 3:
Fretting values F (µm) in diesel fuel (WS 1,4 values according to HFRR according to ISO 12 156-1 at 60°C)

Additive introduced	DF1	DF2	DF3	DF4
None	532 (0)	624 (0)	615 (0)	564 (0)
Additive A	389 (50)	375 (50) 363 (100)	399 (75)	358 (200)
Additive B	355 (50)	471 (50) 359 (100)	401 (75)	388 (200)
Additive C	436 (50)	455 (50) 330 (100)	-	435 (200) 453 (250)
Additive D	517 (50)	474 (150) 252 (200)	-	518 (150) 387 (200)
Additiv E	471 (50)	473 (100) 282 (50)		578 (250) 350 (350)
Additive F	-	-	421 (75)	-

The values stated in brackets indicate the respective dose in ppm by volume.

Example 5: Compatibility with lubricating oil

The tendency of an additive to form insoluble precipitates with lubricating oil can be checked by various standardized laboratory tests. Here, the test prescribed by DGMK (Deutsche Wissenschaftliche Gesellschaft für Erdöl, Erdgas und Kohle e.V., Research Board 531 "Aufstellung eines Kriterienkataloges zur

Testung von Lubricity Additiven in Dieselkraftstoffen für den Raffinerieeinsatz", Hamburg 1998) was used. Here, 10 ml of engine oil (CEC RL 189; SAE 15W40) and 10 ml of additive are homogenized in a 500 ml flask. After 72 hours at 90°C, the mixture is cooled and visually assessed. This mixture is made up to 500 ml with diesel fuel and filtered over a 0.8 µm filter (SEDAB specification). The occurrence of gel or sediment and exceeding a filtration time of 300 seconds leads to "fail". "Pass" on the other hand means that the test requirements have been fulfilled.

Table 4 below, containing the results of this test, illustrates the fact that the lubricity enhancers A and B used according to the invention are likely to have no adverse interactions with lubricating oil.

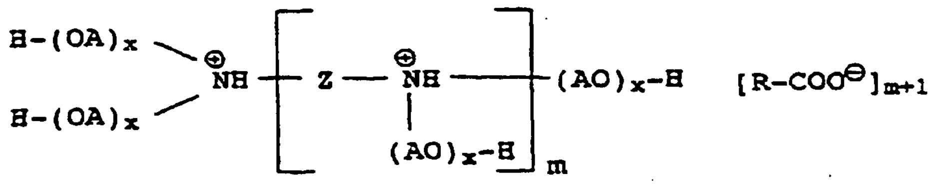
Table 4: Lubricating oil compatibility tests according to DGMK FB 531

Additive	after 72 h at 90°C	Filtration time [sec]	Assessment
None	-	112	-
Additive A	clear	86	Pass
Additive B	clear	89	Pass
Additive D (for comparison)	cloudy	> 300	Fail
Additive G (for comparison)	cloudy, inhomogeneous, gel-like particles	> 1800	Fail

A commercial dimeric fatty acid was used as further comparative additive G.

We claim:

1. The use of fatty acid salts of alkoxylated oligoamines of the formula I



(I)

where

A is an alkylene group of 2 to 8 carbon atoms,

R is C_7- to C_{23}-alkyl or mono- or polyunsaturated C_7- to C_{23}-alkenyl, which may additionally carry hydroxyl groups,

Z is a C_1- to C_8-alkylene group, C_3- to C_8-cycloalkylene group or C_6- to C_{12}-arylene or arylalkylene group,

m is 0 or an integer from 1 to 5 and

the sum of all variables x has a value of from 50 to 300% of (m+3),
as lubricity enhancers for mineral oil products.

2. The use of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in claim 1, in which A is a 1,2-ethylene, 1,2-propylene or 1,2-butylene group.

3. The use of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in claim 1 or 2, in which R is a mono- or polyunsaturated C_{15}- to C_{19}-alkenyl group which may additionally carry hydroxyl groups.

4. The use of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 3, in which Z is a polymethylene group of the formula $-(CH_2)_n-$, where n is from 2 to 6.

5. The use of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 4, in which m is 1 or 2.

6. The use of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 5, in which the sum of all variables x is from 75% to 125% of (m+3).

7. The use of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 6 as lubricity enhancers in gasoline fuels and middle distillates.

8. A process for improving the lubricity of mineral oil products, in particular of gasoline fuels and middle distillates, wherein effective amounts of fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 6 are added to the mineral oil products.

9. An additive concentrate for mineral oil products, in particular for gasoline fuel and middle distillate, containing fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 6 in amounts of from 0.05 to 50% by weight.

10. A mineral oil product, in particular a gasoline fuel or middle distillate composition, containing fatty acid salts of alkoxylated oligoamines of the formula I as claimed in any of claims 1 to 6 in effective amounts.

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